Synthesis and Reactivity of Cyclohexadienyl- and o-Xylylenetricarbonylmanganese Complexes Obtained from the Deprotonation of [Mn(η^6-arene)(CO)$_3$]$^+$ Salts

John W. Hull, Jr.,[1] Kevin J. Roesselet, and Wayne L. Gladfelter*

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

Received March 6, 1992

Following deprotonation of [Mn(η^6-C$_6$Me$_6$)(CO)$_3$]$^+$ with K(O^{t}Bu) to give the known exomethylene cyclohexadienyl complex, a second deprotonation was accomplished using the dual base system K(O^{t}Bu)/KH in THF. The product was the anionic o-xylylene complex K{Mn[η^4-C$_6$Me$_4$(CH$_2$)$_2$](CO)$_3$}. The cyclohexadienyl complex from a single deprotonation of [Mn(η^6-o-xylene)(CO)$_3$]$^+$ was stable only in solution at room temperature, but direct double deprotonation with K(O^{t}Bu)/KH gave the anionic o-xylylene complex K{Mn[η^4-C$_6$H$_4$(CH$_2$)$_2$](CO)$_3$} as a thermally stable solid. Deprotonation of [Mn(η^6-toluene)(CO)$_3$]$^+$, [Mn(η^6-C$_6$H$_5$Et)(CO)$_3$]$^+$, and [Mn(η^6-C$_6$H$_5$-i-Pr)(CO)$_3$]$^+$ salts with excess K(O^{t}Bu) gave the isolable cyclohexadienyl complexes [η^5-C$_6$H$_5$(CH$_2$)]Mn(CO)$_3$, [η^5-C$_6$H$_5$(CHCH$_3$)]Mn(CO)$_3$, and [η^5-C$_6$H$_5$(CMe$_2$)]Mn(CO)$_3$, respectively. All deprotonation products were air and moisture sensitive. Reaction of [η^5-C$_6$H$_5$(CH$_2$)]Mn(CO)$_3$ with HPF$_6$ and Br$_2$ yielded [Mn(η^6-toluene)(CO)$_3$]$^+$ and {Mn[(η^6-C$_6$H$_5$(CH$_2$Br)](CO)$_3$}$^+$, respectively. The anionic o-xylylene complexes gave crystalline solids with ether solvents such as 1,2-dimethoxyethane, diglyme, and dioxane. Mono- and dialkylation of [η^5-C$_6$Me$_5$(CH$_2$)]Mn(CO)$_3$ and K{Mn[η^4-C$_6$Me$_4$(CH$_2$)$_2$](CO)$_3$} with CF$_3$SO$_3$CH$_3$ gave the [Mn(η^6-C$_6$Me$_5$Et)(CO)$_3$]$^+$ and [Mn(η^6-1,2-C$_6$Me$_4$Et$_2$)(CO)$_3$]$^+$ salts, respectively. Attempted alkylation of K{Mn[η^4-C$_6$H$_4$(CH$_2$)$_2$](CO)$_3$} in a similar fashion gave unidentified solids. Treatment of the cyclohexdienyl or o-xylylene complexes with molecular oxygen gave only the parent hydrocarbons, hexamethylbenzene or o-xylene, as the isolated organic products.

Introduction

The synthesis and reactivity of ruthenium stabilized o-xylylene complexes obtained by the double deprotonation of bis(arene)ruthenium complexes has been reported.[2,3] o-Xylylene complexes obtained in this fashion exhibit the unusual feature of a metal binding to the endocyclic diene unit, leaving the exocyclic methylene carbons available as reactive centers.[3]

While addition of nucleophiles to the coordinated arene ring of [Mn(η^6-arene)(CO)$_3$]$^+$ complexes to yield neutral or anionic products has been extensively reported,[4] deprotonation of alkyl side chains of [Mn(η^6-arene)(CO)$_3$]$^+$ systems has been investigated to a much lesser extent.[5] Recently, Eyman's group has reported[6] the synthesis, characterization, and reactivity of the cyclohexadienyl complex [η^5-C$_6$Me$_5$(CH$_2$)]Mn(CO)$_3$ obtained from the monodeprotonation of [Mn(C$_6$Me$_6$)(CO)$_3$]$^+$. In order to further investigate the generality of deprotonation of benzylic protons as a route to stabilized o-xylylenes, we have extended our work to the [Mn(η^6-alkylarene)(CO)$_3$]$^+$ complexes. In an effort to determine both the mode of binding of manganese and the reactivity of the coordinated

o-xylylene ligand, we report the single and double deprotonation of alkylbenzenes coordinated to the tricarbonylmanganese moiety to give neutral cyclohexadienyl and anionic o-xylylene complexes.

Experimental Section

General Information. Literature procedures were used to prepare the (arene)tricarbonylmanganese cations (arene = hexamethylbenzene, o-xylene, toluene, ethylbenzene, and cumene).[4b,7] Methyl trifluoromethanesulfonate was purchased from Aldrich and distilled over P$_2$O$_5$ under nitrogen prior to use. Potassium *tert*-butoxide was purchased from Aldrich, stored and handled in a drybox, and used without further purification. KH was purchased for Alpha-Ventron as a mineral oil suspension, washed numerous times with hexane under nitrogen, dried under vacuum, and stored and handled in a drybox. Tetrahydrofuran, dimethoxyethane, diglyme, dioxane, and diethyl ether were freshly distilled from sodium–benzophenone ketyl.[8] Deep purple solutions of the benzophenone dianion[9,10] were prepared by addition of excess sodium and/or potassium metal to benzophenone in THF. Hexane, pentane, and benzene were distilled over calcium hydride under a nitrogen atmosphere. Tetrahydrofuran-d_8, benzene-d_6, and toluene-d_8 were purchased from Aldrich and distilled under vacuum from molecular sieves. All manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques, unless otherwise noted. Elemental analyses were performed by Galbraith Laboratories. NMR spectra were obtained with a Varian HFT-80 or a Nicolet NTCFT-1180 300-MHz spectrometer. IR spectra were obtained on a Beckman 4250 spectrometer.

Synthesis of [η^5-C$_6$Me$_5$(CH$_2$)]Mn(CO)$_3$ (2a). This procedure is a variation of the deprotonation reported by Eyman and co-workers.[6] [Mn(η^6-C$_6$Me$_6$)(CO)$_3$]PF$_6$ (8.32 g, 18.64 mmol) was weighed into a 500-mL flask equipped with magnetic stir bar, and 150 mL of dry THF was injected under nitrogen. The stirring solution was cooled to –78 °C, while an addition funnel containing solid K(O^{t}Bu) (2.30 g, 20.50 mmol) was fitted onto the flask under

(1) Present address: Agricultural Chemicals Process Research, Dow Chemical U.S.A., 1710 Building, Midland, MI 48674.

(2) Hull, J. W., Jr.; Gladfelter, W. L. *Organometallics* 1982, *1*, 1716.

(3) Hull, J. W., Jr.; Mann, C.; Gladfelter, W. L. *Organometallics*, in press.

(4) (a) Pauson, P. L.; Segal, J. A. *J. Chem. Soc., Dalton Trans.* 1975, 1683. (b) Munro, G. A. M.; Pauson, P. L. *Z. Anorg. Allg.* 1979, *458*, 211. (c) Lamanna, W.; Brookhart, M. *J. Am. Chem. Soc.* 1981, *103*, 989. (d) Brookhart, M.; Pinhas, A. R.; Lukacs, A. *Organometallics* 1982, *1*, 1730. (e) Chung, Y. K.; Choi, H. S.; Sweigert, D. A.; Connelly, N. G. *J. Am. Chem. Soc.* 1982, *104*, 4245. (f) Brookhart, M.; Lamanna, W.; Humphrey, M. B. *J. Am. Chem. Soc.* 1982, *104*, 2117. (g) Brookhart, M.; Lamanna, W.; Pinhas, A. R. *Organometallics* 1983, *2*, 638. (h) Brookhart, M.; Lukacs, A. *Organometallics* 1983, *2*, 649. (i) F. Rose-Munch; Aniss, K. *Tetrahedron Let.* 1990, *31*, 6351.

(5) (a) Johnson, J. W.; Treichel, P. M. *J. Chem. Soc., Chem. Commun.* 1976, 688. (b) Treichel, P. M.; Johnson, J. W. *Inorg. Chem.* 1977, *16*, 749. (c) Treichel, P. M.; Fivizzani, K. P.; Haller, K. J. *Organometallics* 1982, *1*, 931.

(6) LaBrush, D. M.; Eyman, D. P.; Baenziger, N. C.; Mallis, L. M. *Organometallics* 1991, *10*, 1026.

(7) Winkhaus, G.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* 1961, 3807.

(8) Downward, A. J.; Robinson, B. H.; Simpson, J. *Organometallics* 1986, *5*, 1122.

(9) Wooster, C. B. *J. Am. Chem. Soc.* 1928, *50*, 1388.

(10) Murphy, W. S.; Buckley, D. J. *Tetrahedron Lett.* 1969, 2975.

a nitrogen purge. The butoxide was dissolved by injection of 50 mL of dry THF into the addition funnel. The butoxide solution was added dropwise to the cold stirring slurry of the manganese cation over 30 min. After addition was complete, the yellow solution was stirred at −78 °C for another hour, then warmed gradually to room temperature as the THF was removed under vacuum. The yellow solid residue was dried thoroughly under vacuum, then extracted with five 50-mL portions of dry pentane, and filtered through a Schlenk frit into a flask cooled to −78 °C to induce the formation of the crystalline product. The filtrate was reduced in volume under vacuum to about 70 mL, and the cold mother liquor was decanted from the crystals by cannulation under a nitrogen purge. The yellow crystals were rinsed with three portions of cold pentane in this manner. The product was dried under vacuum at +25 °C to give 4.39 g of bright yellow air-sensitive crystals. The mother liquor and combined rinsings were reduced in volume and cooled to −78 °C to give an additional 0.23 g of crystalline product after drying. The combined yield of the cyclohexadienyl complex was 4.62 g (83%). IR (pentane, cm⁻¹): 2015 (vs), 1948 (vs), 1930 (vs), 1588 (m), 807 (m). Proton NMR (ppm, toluene-d_8): δ 3.82 (s, 2 H), 1.86 (s, 3 H), 1.65 (s, 6 H), 1.61 (s, 6 H). High resolution mass spectroscopy. Calcd: 300.0558; Found: 300.0574. Anal. Calcd for C₁₅H₁₇MnO₃: C, 60.01; H, 5.71. Found: C, 60.07; H, 5.70.

Complex **2a** was allowed to stand in 2 mL of dry THF under nitrogen for about 2 weeks. Some decomposition material appeared to form initially, but a dark microcrystalline solid eventually began to form. After about 2 weeks the solution had become colorless. The air-stable solid was collected on a frit, then placed in a test tube and separated from lighter decomposition material by gravity filtration. The resulting black microcrystals were found to be insoluble in a wide variety or organic solvents. IR (KBr, cm⁻¹): 2925 (s), 2855 (m), 2055 (m), 2000 (m), 1995 (m), 1982 (m), 1922 (br), 1852 (vs), 1841 (vs), 1810 (m), 1694 (vs), 1455 (br), 1381 (s), 1260 (w), 1066 (w), 1004 (w), 615 (m).

Synthesis of K{Mn[η⁴-C₆Me₄(CH₂)₂](CO)₃}·x(solvent) (5a). Method A. Dimethoxyethane Solvate. [η⁵-C₆Me₅(CH₂)]Mn(CO)₃ (0.50 g, 1.67 mmol), KH (0.67 g, 16.70 mmol), and K(OᵗBu) (0.37 g, 3.33 mmol) were combined in a drybox as above and stirred magnetically at 0 °C in 50 mL of dry dimethoxyethane (DME) for 1 h and then at +25 °C for another hour. Analysis of this solution by IR spectroscopy indicated complete conversion to the anion as evidenced by the disappearance of the absorptions due to [η⁵-C₆Me₅(CH₂)]Mn(CO)₃ at 2015, 1948, and 1930 cm⁻¹. The yellow solution was filtered through a flame-dried Schlenk frit, and the solvent was removed under vacuum leaving a red-orange oil. This oil was redissolved in 10 mL of dry diethyl ether, filtered under nitrogen, then reduced in volume to a few mL, and cooled to −78 °C to allow crystallization to occur. The mother liquor was removed at −78 °C by cannula, and the yellow solid was washed with several portions of cold ether at −78 °C. The bright yellow crystalline solid was dried at +25 °C under vacuum. A 5-mL portion of ether was added at +25 °C, and initially much of the yellow solid appeared to dissolve, but bright yellow crystals rapidly re-formed. The ether was removed by cannula and the crystals were dried under vacuum and then weighed in a drybox to obtain 0.30 g (42%) of bright yellow crystalline air-sensitive anionic *o*-xylylene complex solvated with a single DME molecule. IR (THF, cm⁻¹): 1933 (vs), 1852 (vs), 1824 (vs), 1798 (m), 1567 (w). The proton NMR results of the dioxane solvated complex are listed below and are identical to those of the DME solvate. ¹³C NMR (ppm, THF-d_8, DME solvate): δ 232.9 (s), 153.8 (s), 92.8 (s), 86.3 (t, *J* = 154.5 Hz), 71.9 (t, *J* = 142.7 Hz, DME), 64.1 (s), 58.7 (q, *J* = 139.6 Hz, DME), 20.4 (q, *J* = 124.3 Hz), 17.0 (q, *J* = 125.6 Hz). Anal. Calcd for C₁₉H₂₈KMnO₅ (1 DME solvate): C, 53.26; H, 6.12; Mn, 12.82. Found: C, 52.98; H, 5.85; Mn, 13.05.

Method B. Dioxane Solvate. [η⁵-C₆Me₅(CH₂)]Mn(CO)₃ (0.20 g, 0.67 mmol), KH (0.03 g, 0.67 mmol), and K(OᵗBu) (0.15 g, 1.33 mmol) were weighed in a drybox into a Schlenk tube containing a stir bar. The Schlenk tube was fitted with a reflux condenser and removed from the drybox, 10 mL of hexane was injected into the reactor, and the slurry was refluxed under nitrogen for 4 h. The resulting air-sensitive yellow powder was collected on a Schlenk frit, rinsed with hexane, then dissolved into rigorously dried dioxane, and filtered to give a yellow orange solution of the anion. The solution was reduced in volume under vacuum to a

few milliliters to allow the formation of bright yellow crystals. The solution was warmed in an oil bath to redissolve the crystals and then cooled slowly to room temperature to give long needlelike crystals. These were collected on an oven-dried frit, washed with hexane, and then dried under vacuum to give 0.21 g of golden-yellow crystals which were stored in a drybox. The yield was approximately 57% based on 2.5 dioxane molecules/anion, as suggested by integration of the ¹H NMR spectrum. Proton NMR (ppm, THF-d_8, dioxane solvate): δ 4.40 (d, *J* = 1.6 Hz, 2 H), 3.84 (d, *J* = 1.6 Hz, 2 H), 3.53 (s, dioxane, ca. 20 H), 2.05 (s, 6 H), 1.67 (s, 6 H).

Method C. Diglyme Solvate. [η⁵-C₆Me₅(CH₂)]Mn(CO)₃ (0.10 g, 0.33 mmol) and KH (0.05 g, 1.33 mmol) were combined in a drybox as above and stirred overnight at +25 °C in 15 mL of THF and 2 mL of diglyme. Analysis of the reaction mixture by IR spectroscopy indicated complete conversion to the anion. The solution was filtered through a Schlenk frit containing oven-dried diatomaceous earth, and the filtrate was reduced in volume to remove most of the THF, leaving mostly diglyme solvent. This concentrated solution was placed in a freezer, and after 3 days large flat crystals had formed. Attempted isolation of these crystals resulted in their redissolving into the solution. Alternatively, the diglyme solution was treated with excess hexane, precipitating a yellow oily material which crystallized on standing. These crystals were collected on a Schlenk frit and rinsed with hexane, but attempts to dry this crystalline material under vacuum led to the loss of crystallinity and the formation of a soft red-orange solid which gradually turned black after a few days of storage in a drybox.

Monodeprotonation of [Mn(η⁶-*o*-xylene)(CO)₃]PF₆. A 10-mL THF solution of K(OᵗBu) (0.29 g, 2.61 mmol) was added quickly dropwise to a 6-mL THF slurry of [Mn(η⁶-*o*-xylene)-(CO)₃]PF₆ (0.51 g, 1.30 mmol) at −78 °C under nitrogen. Stirring was continued at −78 °C for 1 h, after which the insoluble cation had been completely consumed and the solution had turned to a clear orange color. The THF was removed under vacuum while warming to room temperature, leaving a solid yellow residue which was extracted into hexane and filtered under nitrogen. The infrared spectrum of this solution exhibited three strong CO stretches at 2025 (vs), 1958 (vs), and 1943 cm⁻¹ (vs), and a weaker carbon–carbon double bond stretch at 1596 cm⁻¹. A moderate stretch at 2017 cm⁻¹ was also observed, apparently due to an impurity. Evaporation of the hexane gave an insoluble red-yellow solid.

Synthesis of K{Mn[η⁴-C₆H₄(CH₂)₂](CO)₃}·2(dioxane) or K{Mn[η⁴-C₆H₄(CH₂)₂](CO)₃} Unsolvated (5b). Method A (Bis(dioxane) Solvate). A solution of K(OᵗBu) (2.03 g, 18.10 mmol) in 30 mL of THF was added dropwise to a 50-mL THF slurry of [Mn(η⁶-*o*-xylene)(CO)₃]BF₄ (2.00 g, 6.03 mmol) and KH (1.43 g, 35.65 mmol) at −78 °C under nitrogen. After being stirred for 30 min at −78 °C, the bright yellow cloudy solution was warmed to room temperature for an additional 30 min and then filtered through a Schlenk frit under nitrogen. The orange filtrate was reduced in volume under vacuum to about 15 mL; then 20 mL of dry dioxane was injected under nitrogen. The solution was further reduced in volume under vacuum as an insoluble red oil separated from the solution. Further volume reduction and standing resulted in crystallization of the oil. The light orange crystals were collected on a Schlenk frit, rinsed successively with dioxane and excess diethyl ether, and dried under vacuum to give about 1.6 g of crystalline anion as the dioxane solvate. The yield was 58% based on 2.0 dioxane molecules/anion as determined by ¹H NMR spectral integration. The crystals were weighed and stored in a drybox. Anal. Calcd for C₁₉H₂₄KMnO₇ (bis(dioxane) solvate): C, 49.78; H, 5.28; Mn, 11.98. Found: C, 49.51; H, 5.11; Mn, 12.05.

Method B (Unsolvated). A solution of K(OᵗBu) (0.31 g, 2.73 mmol) in 6 mL of THF was added dropwise to a 10-mL THF slurry of [Mn(η⁶-*o*-xylene)(CO)₃]PF₆ (0.35 g, 0.91 mmol) and KH (0.29 g, 7.28 mmol) at −78 °C under nitrogen. The solution was stirred for 15 min at −78 °C and then warmed to 0 °C. As warming of the bright yellow solution took place, evolution of gas was observed. After 30 min at 0 °C, the bubbling had ceased and the solution was filtered through a Schlenk frit under nitrogen. The clear orange filtrate was reduced in volume to a concentrated solution (ca. 3–5 mL); then 20 mL of diethyl ether and 10 mL

of hexane were added, precipitating a light colored solid. The orange solution was filtered again through a Schlenk frit and then reduced in volume under vacuum while cooling as the light yellow microcrystalline anion began to form in solution. The volume was reduced to 7–10 mL and cooled to –78 °C. The mother liquor was removed via cannula away from the light yellow solid, which was washed with three 10-mL portions of diethyl ether and dried under vacuum to give 0.07 g (28%) of the *o*-xylylene anionic complex as an air-sensitive light yellow powder. IR (THF, cm^{-1}): 1942 (vs), 1860 (vs), 1831 (vs), 1805 (m). ^{1}H NMR (ppm, THF-d_8): δ, 4.73 (AA′XX′, 2 H), 4.18 (d, J = 1.9 Hz, 2 H), 3.94 (d, J = 1.9 Hz, 2 H), 3.01 (AA′XX′, 2 H). ^{13}C NMR (ppm, THF): 232.3 (s), 149.5 (s), 88.2 (t, J = 155.0 Hz), 79.0 (d, J = 167.9 Hz), 60.6 (d, J = 153.8 Hz).

Synthesis of [η^5-C$_6$H$_5$(CH$_2$)]Mn(CO)$_3$ (4a). A solution of K(O^{t}Bu) (0.32 g, 2.84 mmol) in 7 mL of THF was added dropwise to a 5-mL THF slurry of [Mn(η^6-C$_6$H$_5$Me)(CO)$_3$]PF$_6$ (0.53 g, 1.42 mmol) at –78 °C under nitrogen. The insoluble cation was rapidly consumed, forming a clear orange solution. After the solution was stirred at –78 °C for 15 min, the solvent was removed under vacuum while the solution was brought to room temperature. The resulting yellow residue was extracted with about 25 mL of dry hexane and filtered under nitrogen to give a clear orange filtrate. This solution was reduced in volume to about 5 mL and then cooled to –78 °C under nitrogen. After a few minutes a bright yellow powder precipitated from solution, and the mother liquor was removed by cannula. The yellow solid was washed with another 5-mL portion of hexane at –78 °C, again removing the solvent by cannula. This was repeated a number of times; then the solid was dried under vacuum at room temperature to give 0.18 g (55%) of the cyclohexanedienyl complex as an air-sensitive yellow powder. This was weighed and stored in a drybox. IR (hexane, cm^{-1}): 2028 (vs), 1966 (vs), 1949 (vs), 1601 (w). A variable intensity absorption at 2018 cm^{-1} was attributed to an impurity. ^{1}H NMR (ppm, C$_6$D$_6$): δ 4.63 (t, J = 5.4 Hz, 1 H), 4.09 (dd, J = 5.4 and 7.5 Hz, 2 H), 3.60 (s, 2 H), 3.47 (d, J = 7.5 Hz, 2 H). Anal. Calcd for C$_{10}$H$_7$MnO$_3$: C, 52.20; H, 3.07. Found: C, 52.23; H, 3.21.

Synthesis of [η^5-C$_6$H$_5$(CHCH$_3$)]Mn(CO)$_3$ (4b). The deprotonation of [Mn(η^6-C$_6$H$_5$Et)(CO)$_3$]PF$_6$ (0.10 g, 0.26 mmol) with K(O^{t}Bu) (0.04 g, 0.31 mmol) was carried out as above. Evaporation of the bright orange hexane filtrate gave the neutral complex as an air-sensitive orange oil. IR (hexane, cm^{-1}): 2021 (vs), 1960 (vs), 1943 (vs), 1648 (w). ^{1}H NMR (ppm, benzene-d_6): δ 4.81 (t, J = 5.3 Hz, 1 H), 4.07 (m, 3 H), 3.48 (d, J = 7.5 Hz, 2 H), 1.30 (d, J = 7.0 Hz, 3 H).

Synthesis of [η^5-C$_6$H$_5$(CMe$_2$)]Mn(CO)$_3$ (4c). The deprotonation was carried out as above from [Mn(η^6-C$_6$H$_5$-i-Pr)(CO)$_3$]PF$_6$ (0.13 g, 0.33 mmol) and K(O^{t}Bu) (0.09 g, 0.7 mmol). The reaction required 35 min before the solid manganese complex was completely consumed, forming a clear red-orange solution. Following the removal of the solvent under vacuum, the resulting red oil was extracted with five 5-mL portions of hexane. These were filtered, reduced in volume to 5 mL, and cooled to –78 °C. After 2 h, a yellow solid had precipitated. The remaining solution was decanted from this material, which was dried under vacuum and stored in a glovebox. The yield was 54.3 mg, or 64%. IR (hexane, cm^{-1}): 2015 (s), 1946 (s), 1935 (vs). Impurity bands at 1980 (w), 1970 (m), 1954 (s), 1921 (m), and 1888 cm^{-1} were sometimes observed. ^{1}H NMR (ppm, C$_6$H$_6$): δ 4.51 (1 H, m), 4.01 (2 H, m), 3.50 (2 H, m), 1.30 (6 H, s). Anal. Calcd for C$_{12}$H$_{11}$MnO$_3$: C, 55.83; H, 4.29. Found: C, 55.97; H, 4.19.

Protonation of [η^5-C$_6$H$_5$(CH$_2$)]Mn(CO)$_3$ (4a). A solution of the cyclohexadienyl complex in 25 mL of hexane was prepared from [Mn(η^6-toluene)(CO)$_3$]PF$_6$ (0.34 g, 0.90 mmol) as described above. A 5-mL amount of HPF$_6$ (40% in water) was added to this solution at room temperature. A fine yellow solid precipitated over 30 min. This material was collected on a frit, washed with water and EtOH, and dried in air. Infrared and NMR spectroscopic analysis identified this compound as the (toluene)manganese tricarbonyl cation 3a. The yield was 0.13 g, or 34%.

Attempted Methylation of [η^5-C$_6$H$_5$(CHCH$_3$)]Mn(CO)$_3$ (4b). A hexane solution of 4b prepared from [Mn(η^6-C$_6$H$_5$Et)(CO)$_3$]PF$_6$ (0.464 g, 1.19 mmol) as described above was cooled to –78 °C. A sample of CF$_3$SO$_3$Me (0.15 mL, 1.3 mmol) was added via syringe and the solution allowed to warm to room temperature overnight.

During this period a tan solid precipitated from the orange solution. This material was collected on a frit under N$_2$ and washed with hexane. The IR spectrum of the precipitate exhibited metal carbonyl stretches at 2080 (m), 2014 (s), and 1936 (s) cm^{-1} in THF solution. The IR spectrum of the yellow filtrate corresponded to that of starting complex 4b; this solution slowly precipitated additional tan solid over time.

The combined solid was redissolved in CH$_3$CN and passed down a silica gel column. IR spectroscopy of the single yellow eluted band indicated strong bands at 2008 (s), 1935 (sh), and 1921 (s) cm^{-1}. NMR spectroscopy gave only broad indistinguishable features.

Reaction of [η^5-C$_6$H$_5$(CH$_2$)]Mn(CO)$_3$ (4a) with Br$_2$. A solution of 4a prepared as above from [Mn(η^6-toluene)(CO)$_3$]PF$_6$ (0.31 g, 0.82 mmol) in 50 mL of hexane was cooled to –78 °C. This clear yellow solution was transferred via cannula over about 30 min into a second solution containing 1.1 mmol of Br$_2$ in 25 mL of hexane at –78 °C. A yellow precipitate began to form immediately. After the addition was complete, the reaction was allowed to warm to room temperature and stirred an additional 2 h. The IR spectrum of the hexane solution at this point indicated that the starting complex 4a had been completely consumed.
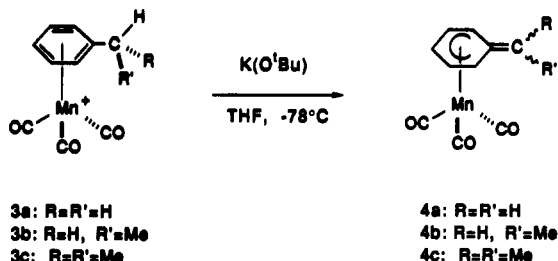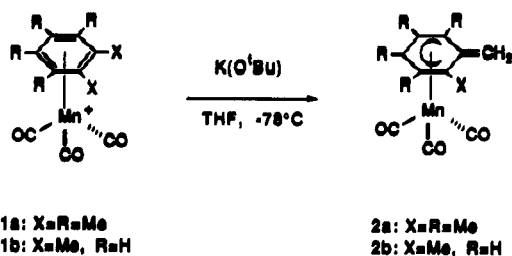
The precipitate was collected on a frit and washed with petroleum ether. The solid was then extracted with 5 mL of water to yield a clear golden-yellow solution and some orange insoluble material shown to be a mixture of Mn(CO)$_5$Br and [Mn(CO)$_4$-(μ-Br)]$_2$ by IR spectroscopy. The aqueous solution was treated with 3 mL of HPF$_6$ (40% in water), precipitating a yellow solid. After the solution was stirred for 10 min, this material was collected on a frit, washed with EtOH, and Et$_2$O, and dried air, giving 0.072 g of 8 as the PF$_6^-$ salt (20%). IR (CH$_3$CN, cm^{-1}): 2080 (s), 2026 (s). ^{1}H NMR (ppm, CD$_3$CN): δ 6.75–6.40 (5 H, m), 4.52 (2 H, s). Anal. Calcd for C$_{10}$H$_7$BrF$_6$MnO$_3$P: C, 26.40; H, 1.55; Br, 17.56. Found: C, 26.67; H, 1.60; Br, 17.34.

Methylation of [η^5-C$_6$Me$_5$(CH$_2$)]Mn(CO)$_3$ (2a). [η^5-C$_6$Me$_5$(CH$_2$)]Mn(CO)$_3$ (0.10 g, 0.33 mmol) was treated with 1.5 mL of freshly distilled CF$_3$SO$_3$Me under nitrogen with magnetic stirring, first at 0 °C and then gradually warming to room temperature. The solution was evaporated under vacuum, and the resulting light-colored residue was dissolved into a few milliliters of water and filtered. Addition of excess NH$_4$PF$_6$ to the aqueous filtrate gave 0.13 g (84%) of methylated complex 6, after collecting on a frit, washing with water and ether, and then drying in air. This product was recrystallized from acetone/ethanol in a freezer to obtain light yellow crystals of [η^6-C$_6$Me$_5$Et]Mn(CO)$_3$PF$_6$. IR (CH$_2$Cl$_2$, cm^{-1}): 2062 (vs), 2005 (vs), 844 (vs). ^{1}H NMR (ppm, acetone-d_6): δ 2.99 (q, J = 7.6 Hz, 2 H), 2.61 (s, 6 H), 2.60 (s, 3 H), 2.57 (s, 6 H), 1.29 (t, J = 7.6 Hz, 3 H). Anal. Calcd for C$_{16}$H$_{20}$F$_6$MnO$_3$P: C, 41.76; H, 4.38. Found: C, 41.31; H, 4.38.

Methylation of K{Mn[η^4-C$_6$Me$_4$(CH$_2$)$_2$](CO)$_3$}. K{Mn[η^4-C$_6$Me$_4$(CH$_2$)$_2$](CO)$_3$} (0.17 g, 0.50 mmol) was treated at 0 °C after evaporation of the THF in which it was prepared, with about 2 mL of freshly distilled CF$_3$SO$_3$CH$_3$. The solution was gradually brought to room temperature and stirred under nitrogen for 30 min. The solution was evaported under vacuum to give a white residue, to which was added wet ether. The solid was collected on a frit and then added to aqueous NH$_4$PF$_6$. This light-colored solid was collected on a frit, washed with water and then with diethyl ether to give 0.06 g of crude dimethylated complex as the PF$_6^-$ salt. The solid was dissolved in acetonitrile and filtered, and then ethanol was added dropwise until precipitation began. The precipitate was removed by filtration and found to be mostly [Mn(C$_6$Me$_6$)(CO)$_3$]PF$_6$. The filtrate was evaporated and found by NMR to be essentially clean diethyl complex. This product was recrystallized from acetone/ethanol to give light yellow crystals of complex 7. IR(CH$_2$Cl$_2$, cm^{-1}): 2063 (vs), 2001 (vs). ^{1}H NMR (ppm, acetone-d_6): δ 2.99 (m, 4 H), 2.62 (s, 6 H), 2.59 (s, 6 H), 1.37 (t, J = 7.6 Hz, 6 H). Anal. Calcd for C$_{17}$H$_{22}$F$_6$MnO$_3$P: C, 43.05; H, 4.68. Found: C, 42.64; H, 4.63.

Attempted Methylation of K{Mn[η^4-C$_6$H$_4$(CH$_2$)$_2$](CO)$_3$} (5b). The crude yellow anion K{Mn[η^4-C$_6$H$_4$(CH$_2$)$_2$](CO)$_3$} (ca. 100 mg) was treated with about 2 mL of neat CF$_3$SO$_3$CH$_3$, freshly distilled from P$_2$O$_5$, under a nitrogen atmosphere for about 30 min. Evaporation of the solution under vacuum gave a light-colored solid, to which was added aqueous NH$_4$PF$_6$. The solid was collected on a frit, washed with water, and dried in air.

Scheme I

1a: X=R=Me
1b: X=Me, R=H

2a: X=R=Me
2b: X=Me, R=H

3a: R=R'=H
3b: R=H, R'=Me
3c: R=R'=Me

4a: R=R'=H
4b: R=H, R'=Me
4c: R=R'=Me
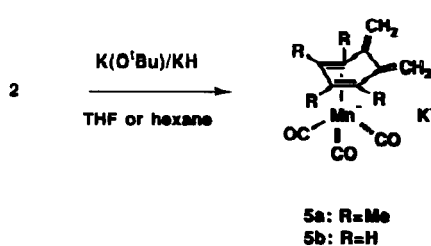
Analysis of this solid by proton NMR indicated that some alkylated and protonated products were present. However, large broad signals were also observed in the proton NMR. The IR spectra of the products in CH₂Cl₂ also exhibited a large unaccountable stretch at 1935 cm⁻¹, as well as two higher-energy stretches due to tricarbonylmanganese cationic species.

Oxidation of [η⁵-C₆Me₅(CH₂)]Mn(CO)₃ (2a). [η⁵-C₆Me₅-(CH₂)]Mn(CO)₃ (about 50 mg) either in the solid state or in hexane solution was treated with molecular oxygen for a period of a few hours. An insoluble brown solid eventually formed, and the hexane solution became completely colorless. The solid was removed by filtration and the hexane evaporated to a white crystalline solid. Proton NMR analysis showed this to be hexamethylbenzene.

Results and Discussion

Monodeprotonation of [Mn(η⁶-arene)(CO)₃]⁺ Complexes. When a THF solution of K(OᵗBu) was added dropwise to a slurry of [Mn(η⁶-hexamethylbenzene)-(CO)₃]PF₆ (1a) in THF at −78 °C, the solution turned rapidly to a yellow color as the insoluble hexamethylbenzene complex was consumed. The resulting neutral cyclohexadienyl complex 2a was isolated in 83% yield as an air- and moisture-sensitive yellow solid (Scheme I). The product was identical to that obtained by Eyman and co-workers using KH as the base.[6] The cyclohexadienyl ligand in 2a[6] also has precedent in Astruc's iron complex Fe(η⁵-C₅H₅)(η⁵-C₆Me₅CH₂)[11] and the previously reported ruthenium analogue [Ru(η⁵-C₆Me₅CH₂)(η⁶-C₆Me₆)]PF₆.[2,3]

The monoalkyl complexes 3 of toluene, ethylbenzene, and cumene were also deprotonated with K(OᵗBu) in THF to give the corresponding cyclohexadienyl complexes 4 (Scheme I). Complexes 4a and 4c were isolated as air-sensitive yellow solids, while 4b was obtained as an air-sensitive oil. Cyclohexadienyl complexes 4 were characterized by their IR and ¹H NMR spectra and by elemental analyses in the case of 4a and 4c. Complex 4b was not obtained in sufficient purity for elemental analysis but exhibited characteristic IR and ¹H NMR spectra for the neutral exomethylene complexes. The IR spectra of exomethylene complexes 2 and 4 in hexane or pentane exhibited three strong bands in the carbonyl region around 2020 and 1930–1960 cm⁻¹ and a weak band characteristic

Scheme II

5a: R=Me
5b: R=H

of the exomethylene ligand in the C=C stretching region around 1600 cm⁻¹. The proton NMR spectrum of the ring protons of complexes 4 are similar to the spectrum of (η⁵-C₆H₇)Mn(CO)₃,[7] with the exception that the 2,6 protons of 4 are shifted downfield by over 1 ppm compared to (η⁵-C₆H₇)Mn(CO₃), due probably to the adjacent exocyclic carbon–carbon double bond. The protons in position 4 of complexes 4 exhibit a triplet around 4.7 ppm, the 3,5 protons exhibit a multiplet around 4.1 ppm, and the 2,6 protons appear as a doublet around 3.5 ppm. The exocyclic protons of 4a appear as a singlet at δ 3.60 ppm compared to δ 3.85 ppm for the permethylated complex 2a.[6] The nonmethylated neutral complexes 4 were unstable at elevated temperatures; mass spectra containing the parent ion could not be obtained. Complex 4a, however, was stored in an inert atmosphere at room temperature as a stable bright yellow powder for an extended period of time.

Monodeprotonation of the *o*-xylene complex 1b with K(OᵗBu) gave the cyclohexadienyl complex 2b (Scheme I), which could not be isolated in pure form but was stable in a dilute hexane solution and gave an IR spectrum characteristic of the other neutral Mn(CO)₃ complexes reported here. Attempts at isolating 2b by precipitation from hexane at low temperature gave a yellow solid which melted below 0 °C during warming to give an unstable red oil.

Two equivalents of K(OᵗBu) were required for complete deprotonation of the mono- or dialkyl complexes 3 and 1b (Scheme I), and except for 3c the cationic starting materials were rapidly consumed under these conditions. Deprotonation of the cumene complex 3c was slower, requiring 35 min for complete consumption of the insoluble cation at −78 °C. Another unidentified neutral complex was observed by infrared analysis when only one equivalent of K(OᵗBu) was used. This may arise from the coupling of neutral cyclohexadienyl product with unreacted cationic starting material, but no attempts to isolate or characterize additional unknown species were made.

An example of a coordinated nonmethylated benzyl ligand such as is observed in complexes 4 (Scheme I) has been reported by Astruc and co-workers,[12] but most of the reported examples are with the fully methylated ring.[2,6,11,13] The possibility of stabilization of this ligand using a tricarbonyliron species has been postulated.[14] The free benzyl radical can be characterized in a matrix at low temperatures.[15] The isolation of stable cyclohexadienyl complexes such as 4 suggests a potential method for functionalization of the benzylic position of aromatic systems such as multiple alkylations[16] or ring functionalization.[17]

(11) Astruc, D.; Hamon, J. R.; Roman, E.; Michaud, P. *J. Am. Chem. Soc.* 1981, *103*, 7502.

(12) Astruc, D.; Roman, E. E.; Hamon, J. R.; Batail, P. *J. Am. Chem. Soc.* 1979, *101*, 2240.
(13) Hamon, J. R.; Astruc, D.; Roman, E.; Batail, P.; Mayerle, J. J. *J. Am. Chem. Soc.* 1981, *103*, 2431.
(14) Hoffmann, R.; Hofmann, P. *J. Am. Chem. Soc.* 1976, *98*, 598.
(15) Migirdicyan, E.; Baudet, J. *J. Am. Chem. Soc.* 1975, *97*, 7400.
(16) (a) Hamon, J. R.; Saillard, J. Y.; Beuze, A. L.; McGlinchey, M. J.; Astruc, D. *J. Am. Chem. Soc.* 1982, *104*, 7549. (b) Astruc, D. *Top. Curr. Chem.* 1991, *160*, 47.

o-Xylylene Complexes. When the permethylated cyclohexadienyl complex 2a was treated with an excess of the dual base system K(O^{t}Bu)/KH in an ether solvent or in warm hexane, 2a was consumed and a second deprotonation was effected. The resulting product exhibited an infrared spectrum characteristic of an anionic metal tricarbonyl system,[4g] giving bands at 1933 (vs), 1852 (vs), 1824 (vs), and 1798 cm^{-1} (m) in the carbonyl region and a weak band at 1567 cm^{-1}. The anionic complex was isolated and characterized by IR and NMR spectroscopies and elemental analysis as the *o*-xylylene complex 5a (Scheme II). The addition of various ether solvents to the reaction mixture allowed the isolation of 5a as a purified crystalline solid in the form of a dioxane or dimethoxyethane solvent. The DME solvate of 5a was recrystallized from diethyl ether. No diethyl ether was ever incorporated into the crystals. The diglyme solvate formed crystals in solution, but we were unable to isolate them in a stable form. When diglyme was present or used as solvent, KH alone was found to deprotonate 2a slowly to the anion 5a. Although the reaction required two to three days for completion, this represented a route to prepare the *o*-xylylene anion in the absence of excess soluble salts because KH could be readily removed by filtration. The diglyme solvate of 5a, however, was not stable as an isolated crystalline solid. The dioxane or dimethoxyethane solvates are bright yellow highly crystalline solids and could be stored in a dry inert atmosphere for extended periods with no visible signs of decomposition.

The direct double deprotonation of *o*-xylene complex 1b with an excess of K(O^{t}Bu)/KH in THF at −78 °C gave a bright clear yellow solution of the anionic *o*-xylylene complex 5b, which exhibited CO stretching frequencies of 1942 (vs), 1860 (vs), 1831 (vs), and 1805 cm^{-1} (m) in the IR spectrum. The infrared spectrum of 5b is nearly identical to that of permethylated anion 5a, the only difference being a small shift to higher energy observed in the CO stretching frequencies. This is consistent with the absence of electron-donating methyl groups on the ring. Removal of the filtered THF solvent gave 5b as a bright yellow air-sensitive solid which was washed with benzene or diethyl ether to remove excess K(O^{t}Bu). Use of the BF$_4$$^-$ counterion of 1b was sometimes found to be an advantage over the PF$_6$$^-$ salt in direct deprotonation to 5b, due to the lower solubility of KBF$_4$ in THF. This byproduct could be easily removed by filtration. Addition of dioxane to the THF solution of the anion resulted in the isolation of light orange crystals as the bis(dioxane) solvate of 5b. This anion was a thermally stable solid, either in solvated or unsolvated form, under oxygen- and moisture-free conditions. The successful preparation and characterization of nonmethylated *o*-xylylene complex 5b (Scheme II) stands in contrast to the ruthenium systems, where a stable nonmethylated *o*-xylylene complex was never successfully isolated.[3]

The carbonyl region of the infrared spectrum of anions 5 in THF was slightly more complicated than expected for a tricarbonylmanganese system.[4c] We attribute these differences to ion pairing effects.

The binding of the metal center to the endocyclic (ring) diene unit of complexes 5 was established by NMR spectroscopy. From the proton NMR spectra of doubly deprotonated complexes 5, the exomethylene protons exhibit two upfield doublets in the 3.8–4.4 ppm range. The two sets of ring protons of 5b appear as two doublets of

(17) Pauson, P. L.; Segal, J. A. *J. Chem. Soc., Dalton Trans.* 1975, 1677.

Scheme III
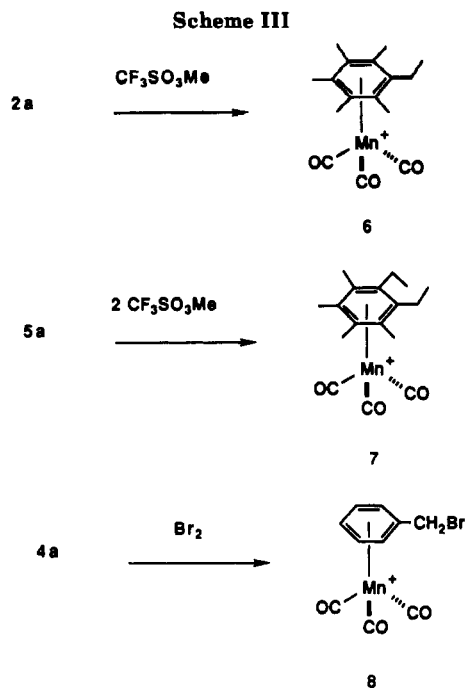
doublets at 4.73 and 3.01 ppm, an upfield shift indicative of an increasing negative charge on the metal center compared to the neutral or cationic precursors. The ^{13}C NMR resonances of the exomethylene carbons also confirm the endocyclic mode of binding, exhibiting a triplet of 86.3 and 88.2 ppm respectively for 5a and 5b in the undecoupled spectrum. This is compared to a value of 89.04 ppm reported for the neutral ruthenium analogue.[2] The noncomplexed pair of ring carbons exhibits singlets at 153.8 and 149.5 ppm for 5a and 5b, respectively. The two sets of ring carbons of the coordinated diene unit of anions 5 gave two singlets at 92.8 and 64.1 ppm for 5a and two doublets at 79.0 and 60.6 ppm for 5b in the undecoupled ^{13}C NMR spectrum. The same set of carbon atoms for the neutral ruthenium analogue[2] exhibited singlets at 84.9 and 60.3 ppm.

While the active deprotonating species to prepare the anions 5 is soluble K(O^{t}Bu), the use of excess KH forces the equilibrium to the right by consuming *tert*-butanol. Although use of catalytic amounts of K(O^{t}Bu) should be feasible, stoichiometric quantities in the presence of excess KH gave much faster and more complete deprotonations to the *o*-xylylene anions 5. The reactions carried out at 0 °C or warmer could be monitored visually with the cessation of bubbling, presumably the evolution of hydrogen gas, indicating completion of the reaction. With this system the anions could be formed even in a nonpolar hydrocarbon solvent such as hexane, at reflux temperatures.

Reactivity. The nucleophilic character of the exocyclic methylene carbons of complexes such as 2a and 5a has been well established.[2,3,6,16] The permethylated complexes 2a and 5a were alkylated at the exomethylene positions by treatment with an excess of CF$_3$SO$_3$CH$_3$ to give the ethylpentamethylbenzene and diethyltetramethylbenzene complexes 6 and 7, respectively (Scheme III). The methylation of 2a occurred cleanly in an 84% isolated yield. Eyman's group reported[6] the iodo-complexed analogue of 6 obtained by treating 2a with methyl iodide. Alkylation of anion 5a occurred with neat CF$_3$SO$_3$CH$_3$ (Scheme III) to give a mixture of dialkylated, monoalkylated, monoprotonated, and diprotonated tricarbonylmanganese products. The major product was dimethylated complex 7 (Scheme III), which was separated from the other

products by fractional crystallization from acetonitrile/ethanol. Interestingly, the methylene protons of the ethyl groups on 7 are diastereotopic and give rise to a complex pattern in the 300-MHz proton NMR spectrum. This arises from differentiation of the two ligand faces by coordinated tricarbonylmanganese.[18]

The alkylation chemistry of anion **5b** stands in contrast to the permethylated system. Treatment of **5b** with excess CF₃SO₃CH₃ gave a light-colored solid product which was not readily identified by IR or NMR spectroscopic analysis. The failure of anion **5b** to give a single alkylation product analogous to the permethylated system indicates that additional alkylation sites on the coordinated ring or the metal center itself may exist. Alkylation of a coordinated manganese center has been reported with a coordinated cyclohexadiene system.[4g]

The appearance of protonated products from reactions of anions **5** was a routine difficulty because protonation of the anion at one of the methylene carbons was extremely facile. Handling of the anionic complexes in solution required the use of rigorously dried ether solvents which had been dried over the deep purple colored benzophenone *dianion*.[9,10] By proton NMR analysis, a solution of **5a** in THF-d_8 which had been vacuum distilled from molecular seives indicated that the anion was partially protonated back to **2a**. By contrast, a ¹³C NMR spectrum of **5a** taken in nondeuterated THF which had been freshly distilled from benzophenone dianion showed no trace of protonation to the neutral complex **2a**.

Although much less reactive than the anions, the exomethylene cyclohexadienyl complexes did react with electrophilic reagents. The protonation of cyclohexadienyl complex **4a** with aqueous HPF₆ gave the cationic toluene complex **3a** in a 34% isolated yield as the PF₆⁻ salt. A similar protonation of **2a** with NH₄PF₆ was reported.[6] Treatment of **4a** with bromine gave the bromomethyl complex **8**, which was characterized by IR and NMR spectroscopies and elemental analysis. Eyman's group reported[6] a similar iodination of **2a**.

o-Xylylene anions **5a** and **5b** were readily oxidized in solution by molecular oxygen, giving the parent hydrocarbons hexamethylbenzene and *o*-xylene, respectively, as the major organic products, along with additional organic products of uncertain composition by mass spectral analysis.

Cyclohexadienyl complex **2a** in solution or as a solid readily decomposed in the presence of oxygen, giving hexamethylbenzene as the sole organic product. Complex **2a** was found to be unstable in THF solution over a period of days, even under an inert atmosphere, giving stable black crystals of undetermined composition which were insoluble in a variety of solvents.

OM9201223

(18) Iverson, D. J.; Hunter, G.; Blount, J. F.; Damewood, J. R., Jr.; Mislow, K. *J. Am. Chem. Soc.* **1981**, *103*, 6073.

Deprotonation of Rhenium Terminal Acetylide Complexes of the Formula (η⁵-C₅R₅)Re(NO)(PPh₃)(C≡CH): Generation and Reactivity of Rhenium/Lithium C₂ Complexes

James A. Ramsden, Weiqing Weng, and J. A. Gladysz*

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

Reactions of methyl complexes (η⁵-C₅R₄R′)Re(NO)(PPh₃)(CH₃) (R/R′ = H/H, H/CH₃, CH₃/CH₃) with HBF₄·OEt₂, chlorobenzene, and R″C≡CH (R″ = H, CH₃) give terminal alkyne complexes [(η⁵-C₅R₄R′)-Re(NO)(PPh₃)(R″C≡CH)]⁺BF₄⁻ (72–87%). When R″ = CH₃, equilibria with methylvinylidene complexes [(η⁵-C₅R₄R′)Re(NO)(PPh₃)(=C=CHCH₃)]⁺BF₄⁻ can be effected at 90–65 °C (75–99% conversion). Treatment of the alkyne or vinylidene complexes with *t*-BuO⁻K⁺ gives acetylide complexes (η⁵-C₅R₄R′)-Re(NO)(PPh₃)(C≡CR″) (R/R′/R″: 1, H/H/H; 3, H/H/CH₃; 11, H/CH₃/H; 12, H/CH₃/CH₃; 2, CH₃/CH₃/H; 17, CH₃/CH₃/CH₃; 81–94%). Reactions of 1 with 1.0 and 2.0 equiv of *n*-BuLi give the lithiated complexes (η⁵-C₅H₅)Re(NO)(PPh₃)(C≡CLi) and (η⁵-C₅H₄Li)Re(NO)(PPh₃)(C≡CLi), respectively, as assayed by ³¹P NMR and subsequent conversion with CH₃I to 3 and 12. Reaction of 1 with 2.0 equiv of *n*-BuLi and Ph₃SnCl gives the stannylated complex (η⁵-C₅H₄SnPh₃)Re(NO)(PPh₃)(C≡CSnPh₃) (49%), which upon silica gel chromatography yields (η⁵-C₅H₄SnPh₃)Re(NO)(PPh₃)(C≡CH). Reaction of 2 with *n*-BuLi gives (η⁵-C₅(CH₃)₅)Re(NO)(PPh₃)(C≡CLi), as assayed by subsequent reactions with CH₃I, D₂O, Me₃SiCl, and Ph₃SnCl to give 17 (95%), 2-*d*₁ (88%; 86–89% labeled), (η⁵-C₅(CH₃)₅)Re(NO)(PPh₃)(C≡CSi(CH₃)₃) (86%), and (η⁵-C₅(CH₃)₅)Re(NO)(PPh₃)(C≡CSnPh₃) (45%).

Transition-metal auxiliaries offer abundant possibilities for modifying the acid/base properties of carbon–hydrogen bonds. Accordingly, diverse types of carbanions have been generated within a metal coordination sphere.[1–3] Their